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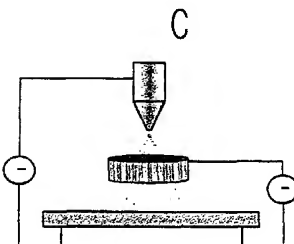
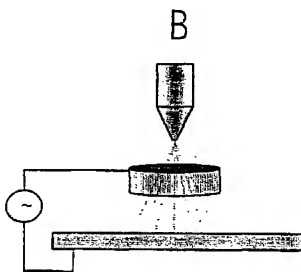
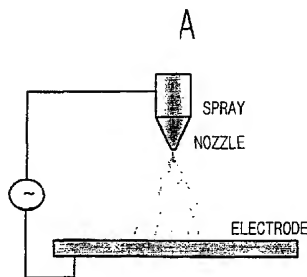
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(54) Title: A LITHIUM SECONDARY BATTERY COMPRISING A POROUS POLYMER SEPARATOR FILM FABRICATED BY A SPRAY METHOD AND ITS FABRICATION METHOD



(57) Abstract: The present invention provides a lithium secondary battery and its fabrication method. More particularly, the present invention provides a lithium secondary battery comprising a porous polymer separator film and its fabrication method, wherein the porous polymer separator film is fabricated by the following process : a) melting at least one polymer or dissolving at least one polymer with an organic solvent to obtain at least one polymeric melt or at least one polymeric solution; b) adding the obtained polymeric melt or polymeric solution to barrels of a spray machine; and c) spraying the polymeric melt or polymeric solution onto a substrate using a nozzle to form a porous separator film. The lithium secondary battery of the present invention has advantages of better adhesion with electrodes, good mechanical strength, better performance at low and high temperatures, and better compatibility with an organic electrolyte solution of a lithium secondary battery.



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**A LITHIUM SECONDARY BATTERY COMPRISING A POROUS
POLYMER SEPARATOR FILM FABRICATED BY A SPRAY METHOD
AND ITS FABRICATION METHOD**

5

TECHNICAL FIELD

The present invention relates to a lithium secondary battery comprising a porous polymer separator film fabricated by a spray method, and to its fabrication method.

10

BACKGROUND ART

Recently electronic apparatus are becoming miniaturized and light-weighted, and accordingly research for the development of energy sources having high density and high energy is being performed intensively. A lithium secondary battery has been proposed as one energy source in the aspect that the higher integration of energy is possible because the molecular weight of lithium used in a lithium secondary battery is very low, but its density is relatively high.

The early lithium secondary batteries were fabricated by using metallic lithium or a lithium alloy as an anode. However, the cycle characteristic of the secondary battery using metallic lithium or a lithium alloy is lowered significantly due to dendrite formation on the anode as a result of repeated charging and discharging of the battery.

A lithium ion battery is proposed in order to solve the problem caused by the dendrite. The lithium ion battery developed by SONY

Company in Japan and widely used all over the world comprises a cathode active material, an anode active material, an organic electrolyte solution and a separator film.

The separator film functions to prevent internal short-circuiting of the lithium ion battery caused by contacting of a cathode and an anode, and to permeate ions. Separator films generally used at the present time are polyethylene (hereinafter referred to as "PE") or polypropylene (hereinafter referred to as "PP") separator films. However, the lithium ion battery using the PE or PP separator film still has problems such as instability, intricacy of the fabrication process, restriction of battery shape and limitation of capacity. There have been attempts to solve those problems, but there is no clear result until now.

On the contrary, a lithium polymer battery uses a polymer electrolyte having two functions, as a separator film and as an electrolyte, and it is now being viewed with keen interest as a battery being able to solve all of the problems. The lithium polymer battery has an advantage in view of productivity because the electrodes and polymer electrolytes can be laminated in a flat-plate shape and its fabrication process is similar to the fabrication process of a polymer film.

A conventional polymer electrolyte is mainly prepared with polyethylene oxide (hereinafter referred to as "PEO"), but its ionic conductivity is merely 10^{-8} S/cm at room temperature, and accordingly it can not be used commonly.

Recently, a gel or hybrid type polymer electrolyte having an ionic

conductivity above 10^{-3} S/cm at room temperature is being developed.

A polymer electrolyte of a gel type polyacrylonitrile (hereinafter referred to as "PAN") group was disclosed in U.S. Patent No. 5,219,679 to K. M. Abraham *et al.* and U.S. Patent No. 5,240,790 to D. L. Chua *et al.*

5 The gel type PAN group polymer electrolyte is prepared by injecting an organic solvent compound (hereinafter referred to as an "organic electrolyte solution") prepared with a lithium salt and organic solvents, such as ethylene carbonate and propylene carbonate, etc. into a polymer matrix. It has an advantage in that the contact resistance is small in
10 charging/discharging of a battery and desorption of the active materials rarely takes place because the adhesive force of the polymer electrolyte is good, and accordingly adhesion between a composite electrode and a metal substrate is well developed. However, such polymer electrolyte has a problem in that its mechanical stability, namely, its strength, is low
15 because the electrolyte is a little bit soft. Especially, such deficiency of strength may cause many problems in fabrication of electrodes and batteries.

A polymer electrolyte of a hybrid type polyvinylidenedifluoride (hereinafter referred to as "PVdF") group was disclosed in U.S. Patent No.
20 5,460,904 to A. S. Gozdz *et al.* The polymer electrolyte of hybrid type PVdF group is prepared by preparing a polymer separator film having porosity of below submicron and followed by injecting an organic electrolyte solution into the pores. It has advantages in that the compatibility of the hybrid type polymer electrolytes with an organic

electrolyte solution is good, the electrolyte injected into the small pores is not leaked so as to be safe in use and the polymer separator film can be fabricated in the atmosphere because the organic electrolyte solution is injected later. However it has a disadvantage in that the fabrication process is intricate because when the polymer electrolyte is prepared, an extraction process of plasticizers and an impregnation process of the organic solvent electrolyte are required. In addition, it has a serious disadvantage in that a process for forming a thin layer by heating and an extraction process are required in fabrication of electrodes and batteries because although mechanical strength of the PVdF group electrolyte is good, its adhesive force is poor.

Recently a polymer electrolyte of a polymethylmethacrylate (hereinafter referred to as "PMMA") group was described in Solid State Ionics, 66, 97, 105 (1993) by O. Bohnke and G. Frand. The PMMA polymer electrolyte has advantages in that its ionic conductivity is 10^{-3} S/cm at room temperature, and its adhesive force and compatibility with the organic electrolyte solution are good. However, it is not suitable for lithium polymer batteries because its mechanical strength is very poor.

In addition, a polymer electrolyte of a polyvinylchloride (hereinafter referred to as "PVC") group, which has good mechanical strength and has an ionic conductivity of 10^{-3} S/cm at room temperature, was described in J. Electrochem. Soc., 140, L96 (1993) by M. Alamgir and K. M. Abraham. However, its low-temperature characteristic is poor and its contact resistance is high.

SUMMARY OF THE INVENTION

Therefore, an object of the present invention is to provide a new lithium secondary battery having advantages of both a lithium ion battery
5 and a lithium polymer battery.

Another object of the present invention is to provide a lithium secondary battery having good adhesion with electrodes, good mechanical strength, good low- and high-temperature characteristics, and good compatibility with an organic electrolyte solution used for a lithium
10 secondary battery.

The above-described and other objects can be achieved by providing a porous polymer separator film of an ultra fine particulate or fibrous form, or a combination thereof, fabricated by a spray method.

BRIEF DESCRIPTION OF DRAWINGS

15 Figures 1a to 1c illustrate embodiments of a spray method by an electrostatic induction.

Figures 2a and 2b illustrate the fabrication of a porous polymer separator film using a spraying machine.

20 Figures 3a to 3c illustrate process flow for fabricating lithium secondary batteries according to the present invention.

Figure 4 is a graph illustrating charge/discharge characteristics of the lithium secondary batteries of Examples 1-5 and Comparative Examples 1 and 2.

Figures 5a and 5b are graphs illustrating low- and high-temperature characteristics of the lithium secondary batteries of Example 2 and Comparative Example 2.

Figures 6a and 6b are graphs illustrating high-rate discharge characteristics of the lithium secondary batteries of Example 2 and Comparative Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a lithium secondary battery comprising a porous polymer separator film fabricated by a spray method, and to its fabrication method. More particularly, it relates to a lithium secondary battery comprising a cathode active material, an anode active material, an organic electrolyte solution in which a lithium salt is dissolved, and a porous polymer separator film, wherein the porous polymer separator film is characterized as being one fabricated by a spray method.

A porous polymer separator film fabricated by a spray method has a form in which particles or fibers, or a combination thereof with a diameter of 1-3000nm is built up three dimensionally. Due to the small diameter of the fibers, the ratio of surface area to volume and the void ratio are very high compared to those of a conventional separator film. Therefore, due to the high void ratio of the porous polymer separator film, the amount of electrolyte impregnated is large and the ionic conductivity is increased, and due to the large surface area, the contact area with the electrolyte can be increased and the leakage of electrolyte can be minimized in spite of the

high void ratio.

Furthermore, in spite of the fabrication method in particulate or fibrous form or a combination thereof, the fabrication equipment and processes can be simplified and the fabrication time can be shortened because the final product is fabricated in the form of a film directly, and accordingly the economic efficiency is high and as well the fabrication of the film is easy. In addition, because the particles or fibers, or combination thereof are built up to form a structure having pores of effective size, closed pores can not be formed structurally, and there is no possibility of closing the pores during the lamination process applied to fabricate batteries. Furthermore, because DBP, which is used in the conventional process of Bellcore Co. is not used, there is no problem of residual DBP.

The process for fabrication of a porous polymer separator film by a spray method comprises a step of obtaining a polymeric melt or polymeric solution and a step of fabricating a separator film using the obtained polymeric melt or polymeric solution.

The step of obtaining a polymeric melt or polymeric solution can be achieved by heating/melting a polymer or polymer mixture, or dissolving a polymer or polymer mixture in a suitable organic solvent. If a polymer is dissolved in an organic solvent, the possible organic solvent used are not particularly limited on condition that they can dissolve the polymer substantially and be applicable to a spray method. In addition, a solvent which might influence on the characteristics of the battery can even be used, because the solvent is almost completely removed while fabricating

a porous polymer separator by a spray method. The examples of an organic solvent include propylene carbonate, butylene carbonate, 1,4-butyrolactone, diethyl carbonate, dimethyl carbonate, 1,2-dimethoxyethane, 1,3-dimethyl-2-imidazolidinone, dimethylsulfoxide, ethylene carbonate, ethylmethyl carbonate, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, polyethylenesulfolane, tetraethylene glycol dimethyl ether, acetone, alcohol or mixtures thereof.

The dissolving step will now be described in more detail. The polymer and an organic solvent are mixed in a 1:1-1:20 ratio by weight and the resulting mixture is stirred at a temperature range of 20-150°C for 30 minutes to 24 hours to obtain a clear polymeric solution. The temperature and stirring time may be changed in accordance with the types of polymers.

The examples of the polymer used for forming the porous polymer separator film include polyethylene, polypropylene, cellulose, cellulose acetate, cellulose acetate butylate, cellulose acetate propionate, polyvinylpyrrolidone-vinylacetate, poly[bis(2-(2-methoxyethoxyethoxy))-phosphagene], polyethyleneimide, polyethyleneoxide, polyethylenesuccinate, polyethylenesulfide, poly(oxymethylene-oligo-oxyethylene), polypropylene-oxide, polyvinylacetate, polyacrylonitrile, poly(acrylonitrile-co-methylacrylate), polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate), poly-vinylchloride, poly(vinylidenechloride-co-acrylonitrile), polyvinylidenedifluoride, poly(vinylidene fluoride-co-hexafluoropropylene) or

mixtures thereof. However the polymer which may be used is not limited to the above examples and any polymer which can be formed to a separator film by a spray method is suitable.

The step of fabricating a separator film with the obtained polymeric melt or polymeric solution can be achieved by filling the polymeric melt or polymeric solution into a barrel of a spray machine and then spraying the polymeric melt or polymeric solution onto a metal plate or Mylar film electrode using a nozzle at a suitable rate. In order to simplify the process, the polymeric melt or polymeric solution can be sprayed directly onto the electrode.

As illustrated in Figures 1a, 1b and 1c, when spraying the polymeric melt or polymeric solution using a nozzle, the polymeric melt or polymeric solution can be sprayed by electrostatic induction. Examples of spraying by electrostatic induction include the following methods. One method is that a nozzle and an electrode are connected to be each given an electrical potential in order that the polymeric melt or polymeric solution coming out from the nozzle has a static electricity (Figure 1a). Another method is that an additional electrode for electrostatic induction is located between the nozzle and an electrode to charge polymeric melt or polymeric solution sprayed by the nozzle (Figure 1b). Another method combines the above two methods (Figure 1c).

A variety of methods can be applied in fabricating a porous polymer separator film. Examples include a method of spraying the polymeric melts or polymeric solutions all together, and another method of installing the

spraying nozzles separately, followed by spraying the respective polymeric melts or polymeric solutions sporadically and continually to get a multi-layered porous polymer separator film. Figures 2a and 2b illustrate the fabrication of a porous polymer separator film using a spray machine.

- 5 Figure 2a illustrates the fabrication method by spraying all together using a nozzle to get a highly porous polymer separator film, and Figure 2b illustrates the fabrication method by spraying sporadically and continually using separately installed nozzles to get a multi-layered porous polymer separator film.

- 10 The thickness of the porous polymer separator film can be adjusted by changing the spray rate and spray time. Preferably, the thickness of the separator film ranges from 1 μm to 100 μm , more preferably, from 5 μm to 70 μm , and most preferably, from 10 μm to 50 μm . It is preferable that the diameter of the polymer forming the porous polymer separator film is
15 adjusted in the range of 1 nm - 3000 nm. A more preferable diameter range is 10 nm - 1000nm, and the most preferable diameter range is 50 nm - 500 nm.

- The porous polymer separator film fabricated by a spray method can comprise two or more polymers and can be fabricated by the following
20 methods. One method is by heating/melting two or more polymers or dissolving two or more polymers in an organic solvent, filling the resulting melts or solution into a barrel of a spray machine and then spraying the melts or solution using a nozzle to fabricate the porous polymer separator film. Another method is by heating/melting each of two or more polymers

separately or dissolving two or more polymers in an organic solvent respectively, filling the resulting melts or solutions into the separate barrels of a spray machine, and then spraying the respective melts or solutions using nozzles to fabricate the porous polymer separator film.

5 The porous polymer separator film of the present invention can additionally include a filling agent in order to improve the porosity and mechanical strength. Preferable examples of a filling agent are TiO_2 , BaTiO_3 , Li_2O , LiF , LiOH , Li_3N , BaO , Na_2O , MgO , Li_2CO_3 , LiAlO_2 , SiO_2 , Al_2O_3 , PTFE or mixtures thereof. It is preferable that the content of the
10 filling agent is below 20% by weight of the porous separator film.

 Lithium salts used in the lithium secondary battery of the present invention are the same as generally used in the lithium secondary battery, such as LiPF_6 , LiClO_4 , LiAsF_6 , LiBF_4 and LiCF_3SO_3 , and among them LiPF_6 is more preferable. Examples of an organic solvent used in the
15 organic electrolyte solution are ethylene carbonate, propylene carbonate, diethyl carbonate, dimethyl carbonate, ethylmethyl carbonate or mixtures thereof. In order to improve the low-temperature characteristic, an additional solvent, such as methyl acetate, methyl propionate, ethyl acetate, ethyl propionate, butylenecarbonate, γ -butyrolactone, 1,2-dimethoxyethane,
20 1,2-dimethoxy-ethane, dimethylacetamide, tetrahydrofuran or mixtures thereof, can be added to the above organic solvent.

 Typical anode and cathode active materials used in the lithium secondary battery in the prior art can be used in the lithium secondary battery of the present invention. Examples of the anode active material

include graphite, cokes, hard carbon, tin oxide and lithiated compounds thereof, metallic lithium, and lithium alloys. Examples of the cathode active material are LiClO_2 , LiNiO_2 , LiNiCoO_2 , LiMn_2O_4 , V_2O_5 or V_6O_{13} .

The lithium secondary battery of the present invention can further
5 comprise conducting materials and binding agents. The anode and cathode of the lithium secondary battery are typically fabricated by mixing a certain amount of active materials, conducting materials and binding agents with an organic solvent, casting the resulting mixture on both sides of a copper or aluminum foil plate grid, and then drying and compressing
10 all of them.

The present invention relates to a fabrication method of a lithium secondary battery and Figures 3a through 3c illustrate the fabrication process in detail. Figure 3a illustrates a process to fabricate a battery, comprising inserting a porous polymer separator film fabricated by a spray
15 method between an anode and a cathode, making the electrolytes and the electrodes into one body by a certain heat lamination process, inserting the resulting plate into a battery casing after laminating or rolling it, injecting an organic electrolyte solution into the battery casing, and then finally sealing the casing. Figure 3b illustrates a process to fabricate a lithium secondary
20 battery, comprising coating a porous polymer separator film by spraying polymeric melts or polymeric solutions directly onto both sides of a cathode or anode, adhering the electrode having opposite polarity to the coated electrode onto the porous polymer separator film, making the electrolytes and the electrodes into one body by a certain heat lamination process,

inserting the resulting plate into a battery casing after laminating or rolling it, injecting an organic electrolyte solution into the battery casing, and then finally sealing the battery casing. Figure 3c illustrates a process to fabricate a lithium secondary battery, comprising coating a porous polymer separator film by spraying polymeric melts or polymeric solutions directly onto both sides of one of two electrodes and onto one side of the other electrode respectively, adhering the electrodes closely together as the porous polymer separator films are faced to each other, making the electrolytes and the electrodes into one body by a certain heat lamination process, inserting the resulting plate into a battery casing after laminating or rolling it, injecting an organic electrolyte solution into the battery casing, and then finally sealing the battery casing.

Examples

The present invention will be better understood from the below examples, but those examples are given only to illustrate the present invention, not to limit the scope of it.

Example 1

1-1) Fabrication of a porous polymer separator film

20g of polyvinylidene fluoride (Kynar 761) was added to 100g of dimethylacetamide, and the resulting mixture was stirred at room temperature for 24 hours to give a clear polymeric solution. The resulting polymeric solution was filled into the barrel of a spray machine and sprayed on a metal plate using a nozzle at a constant rate, to fabricate a

porous polymer separator film of 50 μm thickness.

1-2) Fabrication of a lithium secondary battery

The porous polymer separator film prepared in Example 1-1 was inserted between a graphite anode and a LiCoO_2 cathode. The resulting plates were cut so as to be 3 cm \times 4 cm in size and laminated. Terminals were welded on to the electrodes and the laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the casing, and the casing was then finally vacuum-sealed to give a lithium secondary battery.

10 Example 2

2-1) 20g of polyvinylidene fluoride (Kynar 761) was added to 100g of dimethylacetamide, and the resulting mixture was stirred at room temperature for 24 hours to give a clear polymeric solution. The resulting polymeric solution was filled into the barrel of a spray machine and sprayed on both sides of a graphite anode using a nozzle at a constant rate, to fabricate a graphite anode coated with porous polymer separator films of 50 μm thickness.

2-2) A LiCoO_2 cathode was adhered onto the porous polymer separator film obtained in Example 2-1. The resulting plate was cut so as to be 3 cm \times 4 cm in size and laminated. Terminals were welded on to the electrodes and the laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the casing, and the casing was then finally vacuum-sealed to give a lithium secondary battery.

Example 3

3-1) 20g of polyvinylidene fluoride (Kynar 761) was added to 100g of dimethylacetamide, and the mixture was stirred at room temperature for 24 hours to give a clear polymeric solution. The resulting polymeric solution was filled into the barrel of a spray machine and sprayed on one side of a
5 LiCoO₂ cathode using a nozzle at a constant rate, to fabricate a LiCoO₂ cathode coated with a porous polymer separator film of 50 μm thickness on one side of it.

3-2) The LiCoO₂ cathode obtained in Example 3-1 was adhered to both sides of the graphite anode obtained in Example 2-1 so as to face the
10 porous polymer separator films to each other. The resulting plate was made into one body by heat lamination at 110°C and then cut so as to be 3 cm × 4 cm in size and laminated. Terminals were welded on to the electrodes and then the laminated plate was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-DMC was injected into the casing, and the
15 casing was then finally vacuum-sealed to give a lithium secondary battery.

Example 4

4-1) 10g of polyvinylidene fluoride (Kynar 761) and 10g of PAN (prepared by Polyscience Company, molecular weight of 150,000) were added to 100g of dimethylacetamide, and the resulting mixture was stirred
20 at 120°C for 24 hours to give a clear polymeric solution. The resulting polymeric solution was filled into the barrel of a spray machine and sprayed on both sides of a graphite anode using a nozzle, which was given 9kV charge, at a constant rate, to fabricate a graphite anode coated with

porous polymer separator films of 50 μm thickness.

4-2) The process described In Example 4-1 was applied to one side of a LiCoO_2 cathode instead of to both sides of a graphite anode, to fabricate a LiCoO_2 cathode coated with porous polymer separator films on one side of it.

4-3) The LiCoO_2 cathode obtained in Example 4-2 was adhered to both sides of the graphite anode obtained in Example 4-1 so as to face the porous polymer separator films to each other. The resulting plate was made into one body by heat lamination at 110°C and then cut so as to be 3 cm \times 4 cm in size and laminated. Terminals were welded on to the electrodes and then the laminated plate was inserted into a vacuum casing. A 1M LiPF_6 solution in EC-DMC was injected into the casing, and the casing was then finally vacuum-sealed to give a lithium secondary battery.

Example 5

5-1) Two polymeric solutions of 20g of polyvinylidene fluoride (Kynar 761) in 100g of dimethylacetamide and 20g of PAN (fabricated by Polyscience Company, molecular weight of 150,000) in 100g of dimethylacetamide were filled into the separate barrels of a spray machine respectively. Then the solutions were sprayed on both sides of a graphite anode using nozzles respectively at a constant rate, to fabricate a graphite anode coated with porous polymer separator films of 50 μm thickness.

5-2) A LiCoO_2 cathode was adhered onto a porous polymer separator film obtained in Example 5-1 and the resulting plate was cut so

as to be 3 cm × 4 cm in size and laminated. Terminals were welded on to the electrodes and then the laminated plate was inserted into a vacuum casing. A 1M LiPF₆ solution in EC-DMC was injected into the casing, and the casing was then finally vacuum-sealed to give a lithium secondary
5 battery.

Comparative Examples

Comparative example 1

A lithium secondary battery was fabricated by laminating electrodes and separator films in order of anode, PE separator film, cathode, PE
10 separator film and anode, inserting the resulting laminated plate into a vacuum casing, injecting a 1M LiPF₆ solution in EC-DMC into the casing, and then finally vacuum-sealing the casing.

Comparative example 2

According to the conventional preparation method of a gel-polymer
15 electrolyte, 9g of a 1M LiPF₆ solution in EC-DMC was added to 3g of PAN, and the resulting mixture was mixed for 12 hours. After mixing, the resulting mixture was heated at 130°C for 1 hour to give a clear polymeric solution. When a 10,000cps viscosity suitable for casting was obtained, the polymeric solution was cast by die-casting to give a polymer electrolyte film.
20 A lithium secondary battery was fabricated by laminating in order of a graphite anode, the electrolyte, a LiCoO₂ cathode, the electrolyte and a graphite anode, welding terminals on to the electrodes, inserting the resulting laminated plate into a vacuum casing, injecting a 1M LiPF₆ solution in EC-DMC into the casing, and then finally vacuum-sealing the

casing.

Example 6

Charge/discharge characteristics of the lithium secondary batteries fabricated in Examples 1 - 5 and Comparative Examples 1 and 2 were tested and Figure 4 shows the results. The tests for obtaining charge/discharge characteristics were performed by the charge/discharge method of, after charging the batteries with a C/2 constant current and a 4.2V constant voltage, discharging with a C/2 constant current. The electrode capacities and life cycles based on the cathode were also tested. Figure 4 shows that the electrode capacities and life cycles of the lithium secondary batteries of Examples 1 - 5 were improved compared to the lithium secondary batteries of Comparative Examples 1 and 2. It is considered that those results came about from the decrease of an interface resistance and the increase of an ionic conductivity by good adherence of the electrodes and the separator film.

Example 7

Low- and high-temperature characteristics of the lithium secondary batteries of Example 2 and Comparative Example 2 were tested and Figures 5a and 5b illustrate the respective results (wherein Figure 5a is for the battery of Example 2 and Figure 5b is for the battery of Comparative Example 2). The tests for obtaining the low- and high-temperature characteristics of the lithium secondary batteries were performed by the charge/discharge method of charging the lithium batteries with a C/2 constant current and a 4.2 V constant voltage, and then discharging with a

C/5 constant current. As depicted in Figures 5a and 5b, the low- and high-temperature characteristics of the lithium secondary battery of Example 2 are better than those of the lithium secondary battery of Comparative Example 2. In particular, it shows that the battery of Example 2 has an outstanding characteristic of 91% even at -10°C .

Example 8

High rate discharge characteristics of the lithium secondary batteries of Example 2 and Comparative Example 2 were tested and Figures 6a and 6b illustrate the results (wherein Figure 6a is for the battery of Example 2 and Figure 6b is for the lithium secondary battery of Comparative example 2). The tests for obtaining the high rate discharge characteristics of the lithium secondary batteries were performed by the charge/discharge method of charging the lithium batteries with a C/2 constant current and a 4.2 V constant voltage, and then discharging by changing the constant current into C/5, C/2, 1C and 2C. As depicted in Figures 6a and 6b, the lithium secondary battery of Example 2 shows capacities such as 99% at C/2 discharge, 96% at 1C discharge and 90% at 2C discharge based on the value at C/5 discharge. However, the lithium secondary battery of Comparative Example 2 shows low capacities such as 87% at 1C discharge and 56% at 2C discharge based on the value at C/5 discharge. Accordingly, it was discovered that the high rate discharge characteristic of the lithium secondary battery of Example 2 is better than that of the lithium secondary battery of Comparative Example 2.

CLAIMS

1. A lithium secondary battery, comprising a cathode active material, an anode active material, a porous polymer separator film and an organic electrolyte solution dissolving a lithium salt, wherein said porous polymer
5 separator film comprises a polymer of particulate or fibrous form, or a combination thereof, having a diameter of 1-3000nm.
2. The lithium secondary battery according to claim 1, wherein the porous polymer separator film is fabricated by a spray method.
- 10 3. The lithium secondary battery according to claim 2, wherein the spray method is a spray method by electrostatic induction.
4. The lithium secondary battery according to claim 1, wherein the
15 porous separator film is fabricated by the following process:
heating/melting a polymer or polymer mixture, or dissolving a polymer or polymer mixture in a suitable organic solvent to obtain a polymeric melt or polymeric solution;
filling the polymeric melt or polymeric solution into a barrel of a spray
20 machine; and
spraying the polymeric melt or polymeric solution using a nozzle.
5. The lithium secondary battery according to claim 1, wherein the porous separator film is fabricated by the following process:

heating/melting two or more polymers for forming a porous polymer separator film respectively or dissolving two or more polymers for forming a porous polymer separator film in an organic solvent respectively to obtain two or more polymeric melts or polymeric solutions;

- 5 filling the polymeric melts or polymeric solutions into different barrels of a spray machine respectively; and
- spraying the polymeric melts or polymeric solutions using nozzles.

6. The lithium secondary battery according to claim 4 or claim 5,
10 wherein the organic solvent for dissolving the polymers is one selected from the group consisting of propylene carbonate, butylene carbonate, 1,4-butyrolactone, diethyl carbonate, dimethyl carbonate, 1,2-dimethoxyethane, 1,3-dimethyl-2-imidazolidinone, dimethylsulfoxide, ethylene carbonate, ethylmethyl carbonate, N,N-dimethylformamide,
15 N,N-dimethylacetamide, N-methyl-2-pyrrolidone, polyethylenesulforane, tetraethylene glycol dimethyl ether, acetone, alcohol and mixtures thereof.

7. The lithium secondary battery according to claim 1, wherein the porous polymer separator film is characterized by having a thickness of 1
20 μm ~ 100 μm.

8. The lithium secondary battery according to claim 1, wherein the polymer for forming the porous polymer separator film is one selected from the group consisting of polyethylene, polypropylene, cellulose, cellulose

acetate, cellulose acetate butylate, cellulose acetate propionate,
 polyvinylpyrrolidone-vinylacetate,
 poly[bis(2-(2-methoxyethoxyethoxy))-phosphagene], polyethyleneimide,
 polyethyleneoxide, polyethylenesuccinate, polyethylenesulfide,
 5 poly(oxymethylene-oligo-oxyethylene), polypropylene-oxide,
 polyvinylacetate, polyacrylonitrile, poly(acrylonitrile-co-methylacrylate),
 polymethylmethacrylate, poly(methylmethacrylate-co-ethylacrylate),
 poly-vinylchloride, poly(vinylidenechloride-co-acrylonitrile),
 polyvinylidene-difluoride, poly(vinylidene- fluoride-co-hexafluoropropylene)
 10 and mixtures thereof.

9. The lithium secondary battery according to claim 1, wherein the
 lithium salt incorporated in the porous polymer separator film is LiPF_6 ,
 LiClO_4 , LiAsF_6 , LiBF_4 or LiCF_3SO_3 .

15

10. The lithium secondary battery according to claim 1, wherein the
 organic solvent used in the organic electrolyte solution is ethylene
 carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate,
 ethylmethyl carbonate or mixtures thereof.

20

11. The lithium secondary battery according to claim 10, wherein the
 organic solvent further comprises methyl acetate, methyl propionate, ethyl
 acetate, ethyl propionate, butylenecarbonate, γ -butyrolactone,
 1,2-dimethoxyethane, 1,2-dimethoxyethane, dimethylacetamide,

tetrahydrofuran or mixtures thereof in order to increase a low-temperature characteristic.

12. The lithium secondary battery according to claim 1, wherein the
5 porous polymer separator film further comprises a filling agent.

13. The lithium secondary battery according to claim 12, wherein the
filling agent is selected from the group consisting of TiO_2 , BaTiO_3 , Li_2O , LiF ,
 LiOH , Li_3N , BaO , Na_2O , MgO , Li_2CO_3 , LiAlO_2 , SiO_2 , Al_2O_3 , PTFE and
10 mixtures thereof, and the amount of the filling agent is below 20% (wherein
0% is excluded) of total weight of the porous polymer separator film.

14. A method for fabricating a lithium secondary battery comprising the
following process:

15 inserting a porous polymer separator film fabricated by a spray
method between an anode and a cathode;

inserting the resulting plate into a battery casing after laminating or
rolling it;

injecting an organic electrolyte solution into the casing; and

20 sealing the battery casing.

15. A method for fabricating a lithium secondary battery comprising the
following process:

inserting a porous polymer separator film fabricated by a spray

method between an anode and a cathode;

making the electrolytes and the electrodes into one body by a heat lamination process;

5 inserting the resulting plate into a battery casing after laminating or rolling it;

injecting an organic electrolyte solution into the battery casing; and sealing the battery casing.

16. A method for fabricating a lithium secondary battery comprising the
10 following process:

coating porous polymer separator films fabricated by a spray method on both sides of an anode or cathode;

adhering an electrode having opposite polarity to the coated electrode closely onto the electrolytes;

15 inserting the resulting plate into a battery casing after laminating or rolling it;

injecting an organic electrolyte solution into the battery casing; and sealing the battery casing.

20 17. A method for fabricating a lithium secondary battery comprising the following process:

coating porous polymer separator films fabricated by a spray method on both sides of an anode or cathode;

adhering an electrode having opposite polarity to the coated

electrode closely onto the electrolytes;

making the electrolytes and the electrodes into one body by a heat lamination process;

inserting the resulting plate into a battery casing after laminating or
5 rolling it;

injecting an organic electrolyte solution into the battery casing; and
sealing the battery casing.

18. A method for fabricating a lithium secondary battery comprising the
10 following process:

coating porous polymer separator films fabricated by a spray
method on both sides of one of two electrodes and on one side of the other
electrode;

adhering the electrodes closely so that the polymer electrolytes are
15 faced to each other;

inserting the resulting plate into a battery casing after laminating or
rolling it;

injecting an organic electrolyte solution into the battery casing; and
sealing the battery casing.

20

19. A method for fabricating a lithium secondary battery comprising the
following process:

coating porous polymer separator films fabricated by a spray
method on both sides of one of two electrodes and on one side of the other

electrode;

adhering the electrodes closely so that the polymer electrolytes are
faced to each other;

making the electrolytes and the electrodes into one body by a heat
5 lamination process;

inserting the resulting plate into a battery casing after laminating or
rolling it;

injecting an organic electrolyte solution into the battery casing; and
sealing the battery casing.

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FIG. 1A

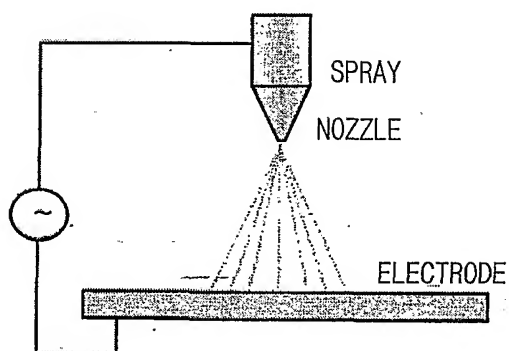


FIG. 1B

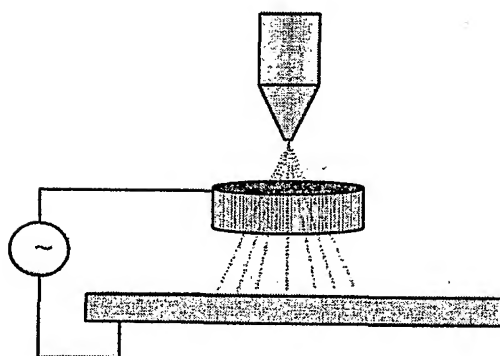
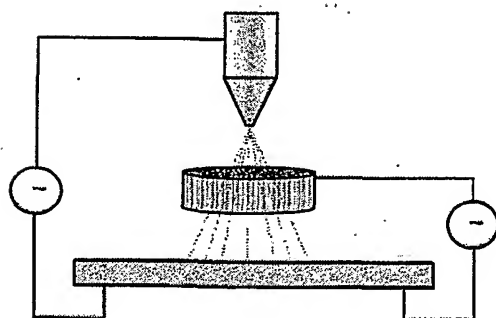


FIG. 1C



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FIG. 2A

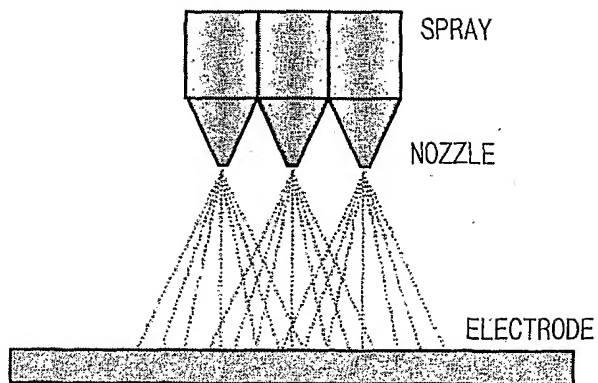
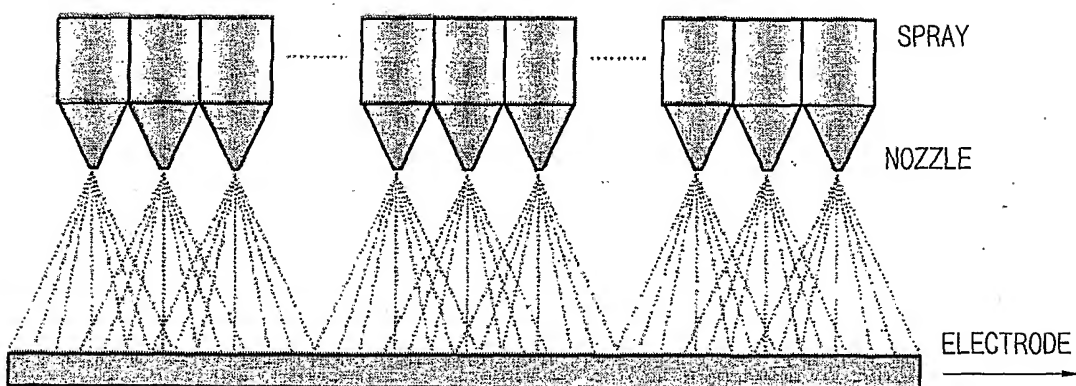


FIG. 2B



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FIG. 3A

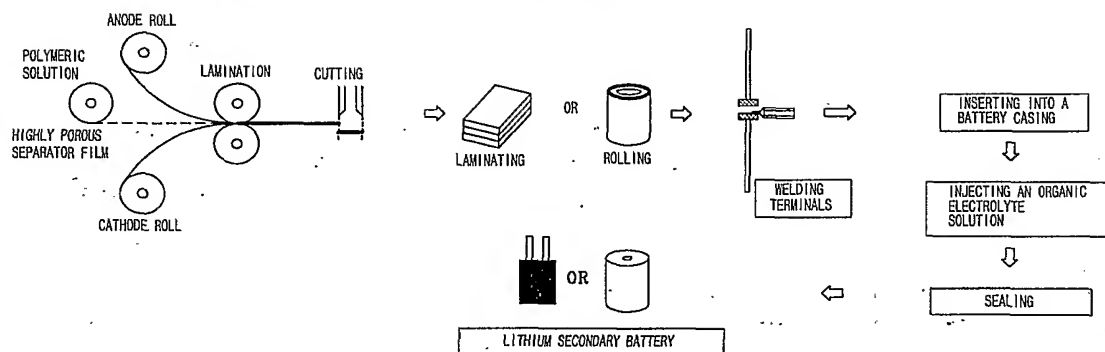


FIG. 3B

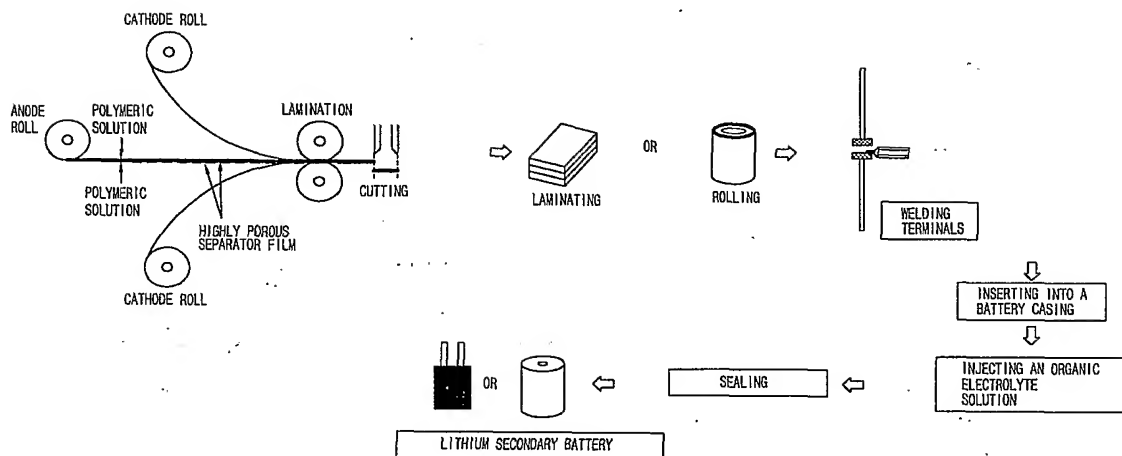
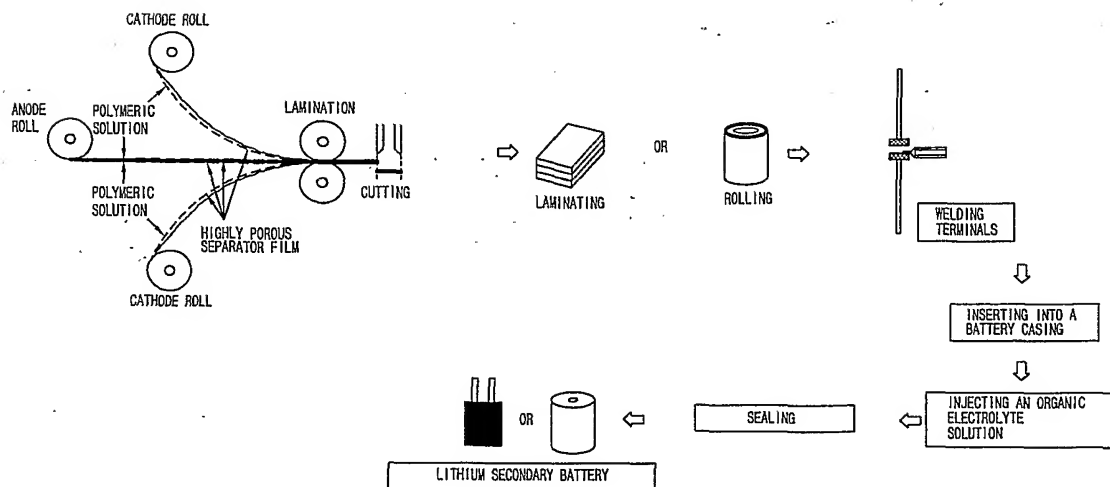
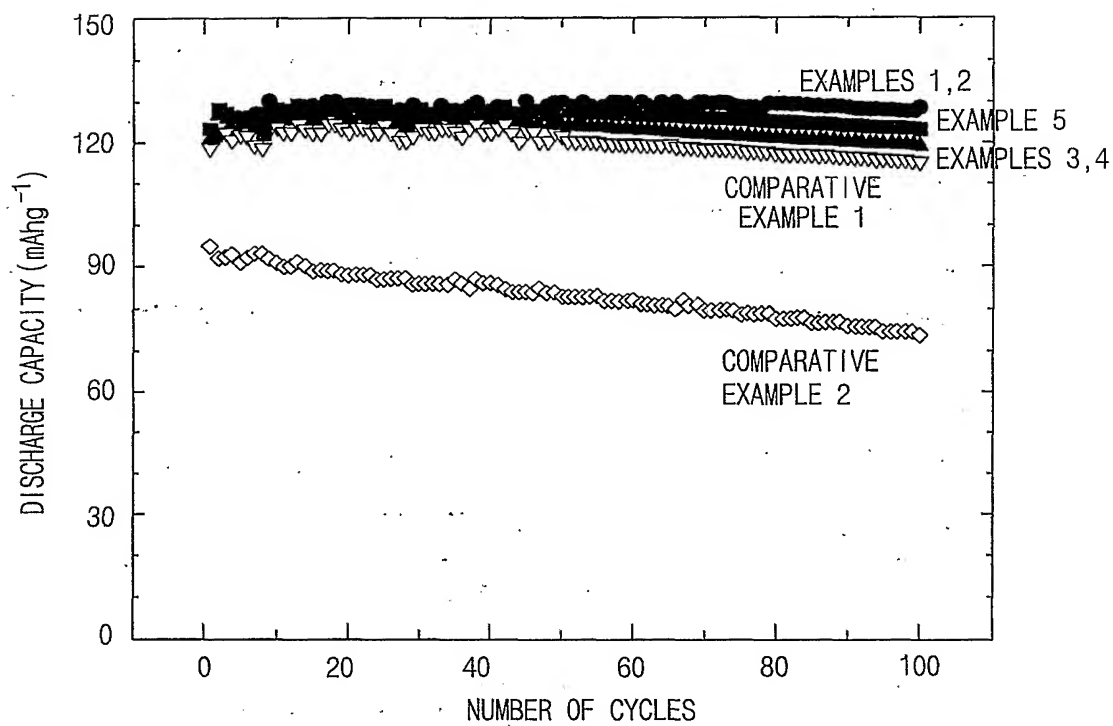


FIG. 3C



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FIG. 4



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FIG. 5A

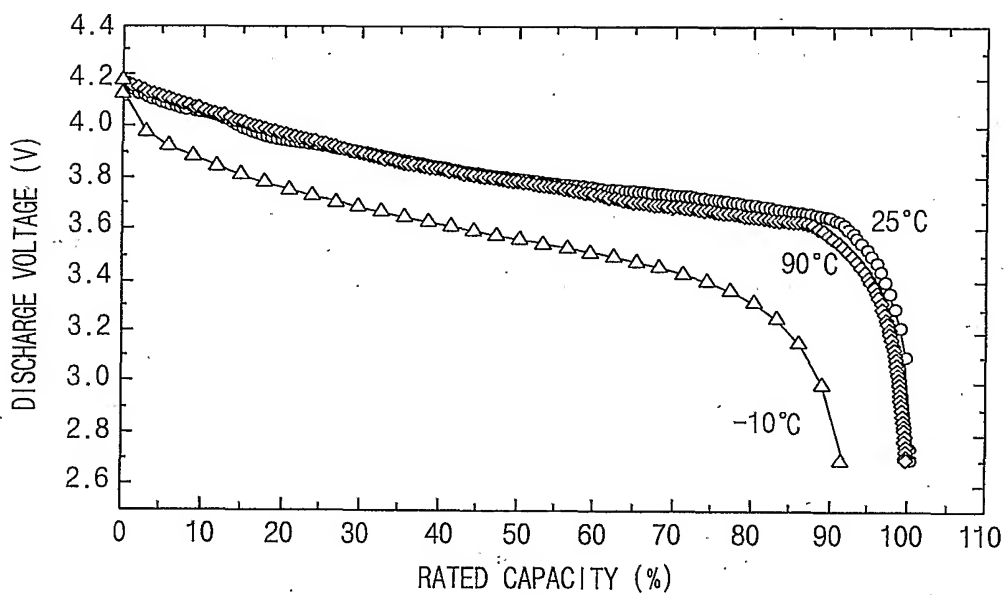
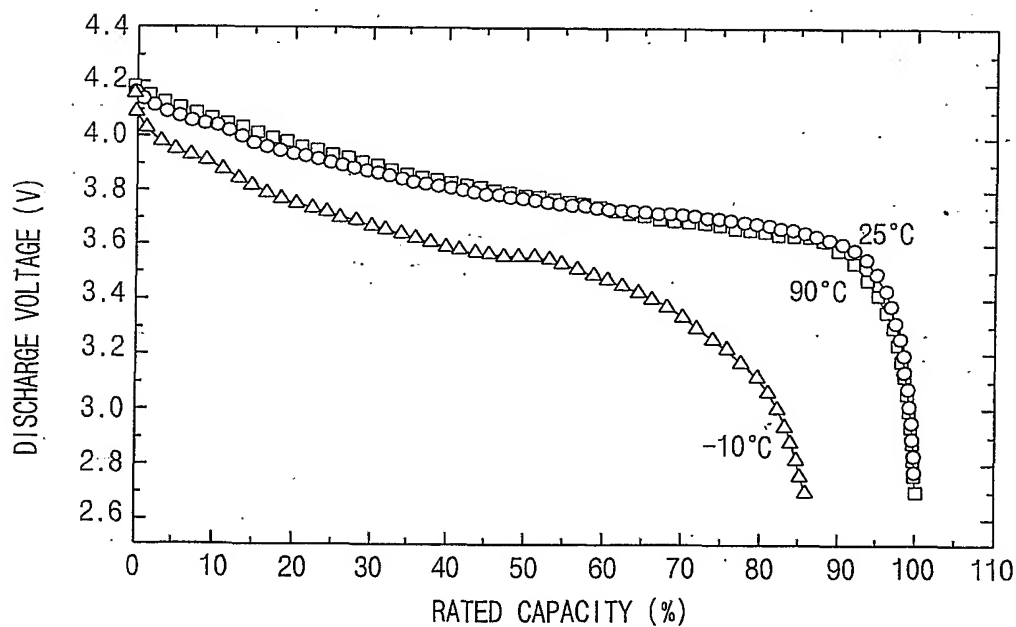


FIG. 5B



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FIG. 6A

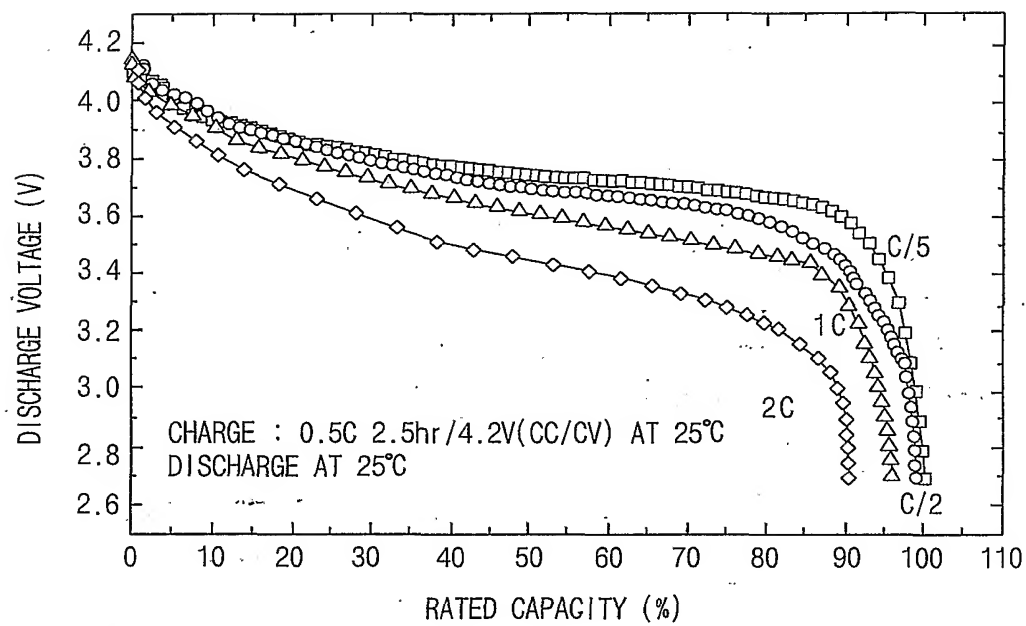
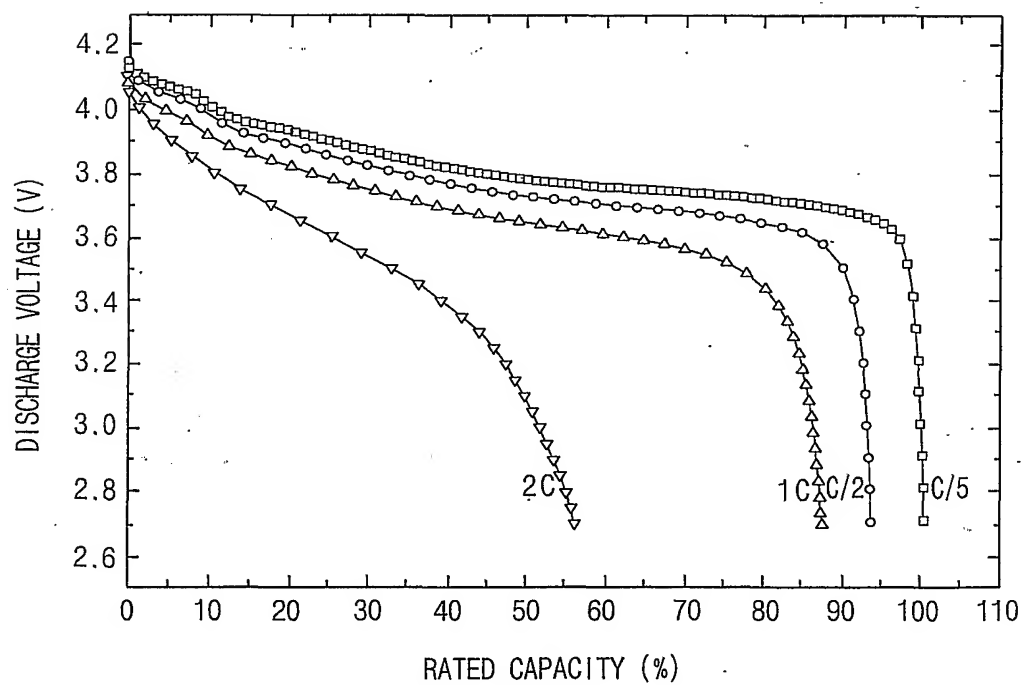


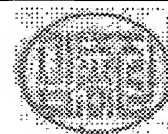
FIG. 6B



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR00/00512

A. CLASSIFICATION OF SUBJECT MATTER		
IPC7 H01M 10/38		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC7 : H01M; D01D; F02M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) USPAT, FPD, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, B1, 08250100 (FUJI PHOTO FILM CO., LTD.) 27 SEPTEMBER 1996 SEE THE WHOLE DOCUMENT	1-13
Y	US, A, 6051175 (POLYMER PROCESSING RESEARCH INST. LTD.) 18 APRIL 2000 SEE ABSTRACT	2-6
Y	US, A, 3925525 (CELANESE CORPORATION) 9 DECEMBER 1975 SEE ABSTRACT, SEE CLAIM1	2-6
Y	US, A, 5296185 (THE DOW JONES CHEMICAL COMPANY) 22 MARCH 1994 SEE THE WHOLE DOCUMENT	2-6
Y	JP, A, 12082498 (NEC CORP.) 21 MARCH 2000 SEE THE WHOLE DOCUMENT	14-19
Y	US, A, 5525443 (MATSUSHITA ELECTRIC IND CO., LTD.) 11 JUNE 1996 SEE THE WHOLE DOCUMENT	10-11
Y	JP, A, 03038226 (ASAHI CHEM IND CO., LTD.) 19 FEBRUARY 1991 SEE THE WHOLE DOCUMENT	2-6
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 21 FEBRUARY 2001 (21.02.2001)		Date of mailing of the international search report 22 FEBRUARY 2001 (22.02.2001)
Name and mailing address of the ISA/KR Korean Industrial Property Office Government Complex-Taejon, Dunsan-dong, So-ku, Taejon Metropolitan City 302-701, Republic of Korea Facsimile No. 82-42-472-7140		Authorized officer KIM, Jong Jin Telephone No. 82-42-481-5730



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR00/00512

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A2, 0398689 (TOKYO SHIBAURA ELECTRIC CO. TOSHIBA BATTERY) 22 NOVEMBER 1990 SEE CLAIM4	9
Y	US, A, 4812375 (US ARMY,) 14 MARCH 1989 SEE THE WHOLE DOCUMENT	1-13
Y	JP, A, 09022724 (TOSHIBA BATTERY CO., LTD.) 21 JANUARY 1997 SEE THE WHOLE DOCUMENT	1-13
Y	JP, A, 60252716 (MITSUBISHI RAYON CO., LTD.) 13 DECEMBER 1985 SEE THE CLAIM	1-13
Y	JP, A, 10208775 (TOSHIBA BATTERY CO., LTD.) 7 AUGUST 1998 SEE THE WHOLE DOCUMENT	14-19